20. Simulation of Micelles and Vesicles of Amphiphilic Block Copolymers by Density Functional Theory(poster presentation,Soft Matter as Structured Materials)

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Simulation of Micelles and Vesicles of Amphiphilic Block Copolymers by Density Functional Theory

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本研究では密度汎関数理論を用いて両親媒性ブロックコポリマー系のミセル・ベシクルのシミュレーションを行った。ブロックコポリマー系のミセル構造はブロックコポリマーの形状や相互作用等に依存して変化する。様々な種類の両親媒性ブロックコポリマー系に対してシミュレーションを行った結果、球状ミセル、円柱状ミセル、ベシクルといったミセル構造が得られた。

1 Introduction

Amphiphilic block copolymer solutions form self-assembling, micellar structures such as micelles or vesicles[1]. The morphologies of the micellar structures depend on the structure of block copolymers or the interaction between the subchains of block copolymers or between the subchain and the solvent. In this work, we performed simulations based on the density functional theory (DF)[2], which is suitable for the real space, large scale simulation.

2 Theory

First we index one polymer species in the system as p, and one subchain in the p-polymer as i. Thus one subchain in the system can be distinguished by the index (p,i). For example, we can write the subchain density for the (p,i) subchain at position $\boldsymbol{r}$ as $\phi_{pi}(\boldsymbol{r})$. In the density functional theory, free energy of the system is expressed as the functional of the density field $\phi_{pi}(\boldsymbol{r})$. We use the following free energy functional model[2].

$$\begin{aligned} F\left[\{\psi_{pi}(\boldsymbol{r})\}\right] = & \sum_{p,ij}\int d\boldsymbol{r}d\boldsymbol{r}'\, 2\sqrt{f_{pi}f_{pj}}A_{p,ij}\mathcal{G}(\boldsymbol{r}-\boldsymbol{r}')\psi_{pi}(\boldsymbol{r})\psi_{pj}(\boldsymbol{r}') \\ & + \sum_{pi}\int d\boldsymbol{r}\, 2f_{pi}C_{p,ii}\psi_{pi}^2(\boldsymbol{r})\ln\psi_{pi}(\boldsymbol{r}) + \sum_{p,i\neq j}\int d\boldsymbol{r}\, 2\sqrt{f_{pi}f_{pj}}C_{p,ij}\psi_{pi}(\boldsymbol{r})\psi_{pj}(\boldsymbol{r}) \\ & + \sum_{pi}\int d\boldsymbol{r}\,\frac{b^2}{6}\left|\nabla\psi_{pi}(\boldsymbol{r})\right|^2 + \sum_{pi,qj}\int d\boldsymbol{r}\,\frac{\chi_{pi,qj}}{2}\psi_{pi}^2(\boldsymbol{r})\psi_{qj}^2(\boldsymbol{r}) \end{aligned} \tag{1}$$

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where $\psi_{pi}(\boldsymbol{r}) \equiv \sqrt{\phi_{pi}(\boldsymbol{r})}$, f_{pi} is the block ratio for the (p,i) subchain, b is the segment size, $\chi_{pi,qj}$ is the χ parameter between the (p,i) and the (q,j) subchains. $\mathcal{G}(\boldsymbol{r}-\boldsymbol{r}')$ is the Green function which satisfies $-\nabla^2\mathcal{G}(\boldsymbol{r}-\boldsymbol{r}') = \delta(\boldsymbol{r}-\boldsymbol{r}')$. $A_{p,ij}$ and $C_{p,ij}$ are the matrices which is independent of $\psi_{pi}(\boldsymbol{r})$. They can be calculated from f_{pi}, b, N_p (polymerization index of the p-polymer) and the topological structure of the p-polymer.

3 Simulation

We minimized free energy functional eq (1) numerically, to get the steady state structures[3]. The DF simulations are carried out for various amphiphilic block copolymer systems (AB diblock copolymer / A homopolymer blends, AB diblock copolymer solutions, ABA triblock linear copolymer / A homopolymer blends, and ABCA tetrablock linear copolymer / A homopolymer blends). Figure 1 and 2 show the results of DF simulations (AB diblock copolymer / A homopolymer blends with different block ratios). We obtained Micellar structures including spherical micelles, cylindrical micelles and vesicles.

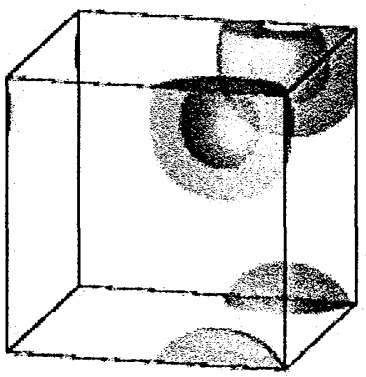

Figure 1: A result of the simulation for the AB diblock copolymer / A homopolymer blend. Isodensity surface for $\phi_{AB,B}(\boldsymbol{r}) = 0.5$ is shown. A vesicle is formed.

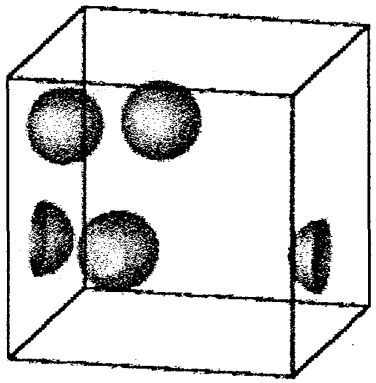

Figure 2: A result of the simulation for the AB diblock copolymer / A homopolymer blend. Isodensity surface for $\phi_{AB,B}(\boldsymbol{r}) = 0.5$ is shown. Spherical micelles are formed

References

[1] A. Choucair and A. Eisenberg, *Euro. Phys. J.*,**10**, 37 (2003).

[2] T. Uneyama and M. Doi, *Macromolecules* **38**, 196 (2005).

[3] T. Uneyama and M. Doi, *Macromolecules* **38**, 5817 (2005).